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(54)【発明の名称】　フッ素化合物含有ガスの処理方法

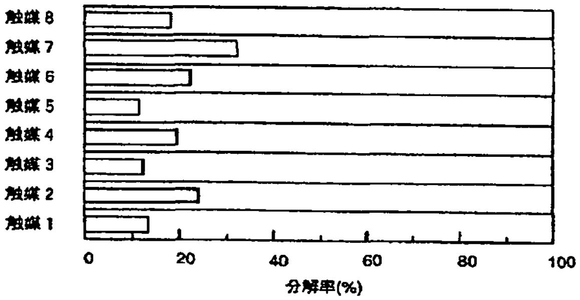
(57)【要約】

【課題】C_2F_6などのフッ素化合物含有ガスを効率良く分解する分解処理方法及び触媒を提供する。

【解決手段】C_2F_6のように炭素を２つ以上含み、かつフッ素原子を含む化合物、もしくは窒素原子とフッ素原子を含む化合物の少なくとも一方を含むガス流を、アルミナ，チタニア，シリカ，ジルコニアの少なくとも一種を含む触媒と、約４００〜約８００℃の温度で、有効量の水蒸気の存在下で接触させて、前記ガス流中のＦをＨＦに転化する。

【効果】フッ素化合物含有ガスを効率良く分解処理することができる。

図　2



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【特許請求の範囲】

【請求項１】炭素を２つ以上含み、かつフッ素原子を含む化合物、もしくは窒素原子とフッ素原子を含む化合物の少なくとも一方を含むガス流を、アルミナ，チタニア，シリカ，ジルコニアの少なくとも一種を含む触媒と約４００～８００℃の温度で、有効量の水蒸気の存在下で接触させて、前記ガス流中のＦをＨＦに転化する工程を含んでなることを特徴とするフッ素化合物含有ガスの処理方法。

【請求項２】請求項１記載の方法において、前記フッ素化合物含有ガスが、炭素を２つ以上含むＣとＦとの化合物、もしくはＮとＦとの化合物であることを特徴とするフッ素化合物含有ガスの処理方法。

【請求項３】請求項１記載の方法において、前記触媒が、さらにＳｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉのうちの少なくとも一成分を含むことを特徴とするフッ素化合物含有ガスの処理方法。

【請求項４】炭素を２つ以上含むＣとＦとの化合物、もしくはＮとＦとの化合物を少なくとも一方を含むガス流を処理する触媒であって、アルミナとチタニアを含み、アルミナが７５ｗｔ％以上９８ｗｔ％以下、チタニアが２５ｗｔ％以下２ｗｔ％以上であることを特徴とするフッ素化合物分解触媒。

【請求項５】請求項４記載の触媒において、さらにＳｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉ，Ｐ，Ｂのうちの少なくとも一成分を含むことを特徴とするフッ素化合物分解触媒。

【請求項６】請求項５記載の触媒において、Ｓｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉ，Ｐ，Ｂの酸化物を、アルミナ－チタニア触媒主量に対し、０．１wt%～１０ｗｔ％で含むことを特徴とするフッ素化合物分解触媒。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、C_2F_6などのフッ素化合物含有ガスを低温で効率良く分解する分解処理方法及び触媒材料に関する。

【０００２】

【従来の技術】C_2F_6などのフッ素化合物ガスは、半導体エッチング材料，半導体洗浄用などに大量に使用されている。しかし、これらの物質は大気中に放出されると、地球の温暖化を引き起こす温暖化物質であることがわかってきた。今後、これらの化合物の使用後の処理に対して、厳しい規制が行われると予想される。

【０００３】ところで、C_2F_6などのガスは、分子構成成分としてフッ素（Ｆ）を多く含有している。フッ素はすべての元素の中で最も電気陰性度が大きく、化学的に非常に安定な物質を形成する。特にC_2F_6などは分子内力が強く、反応性に乏しい物質である。この性質から、分解するには高温が必要であり、大量のエネルギを消費する。また、高温での分解反応は生成するフッ化水素などのガスによる装置材料の腐食速度が大きく、適切な分解処理方法がないのが現状である。

【０００４】分解処理方法として、現在、提案されつつあるのは、高温での燃焼技術である。しかしながらこの方法では、大量の燃料を使用するためエネルギー効率が低く、また、燃焼に伴って生成する１０００℃以上のハロゲン化合物による炉壁の損傷の問題もある。従って、より低温で分解できる技術が必要である。

【０００５】触媒については、これまでに、TiO_2-WO_3触媒が有機ハロゲン化合物の分解用触媒として、特公平6－59388号公報に報告されている。この触媒はTiO_2の０．１～２０ｗｔ％ のＷを含む触媒（原子比にすると、Ｔｉが９２％以上９９．９６％以下、Ｗが８％以下０．０４％以上）であり、ppmオーダーのCCl_4を処理するのに３７５℃で分解率９９％を１５００時間保持していた。有機ハロゲン化合物中で触媒毒としての影響はＣｌだけでなく、むしろＦの方が大きい。該公報では、炭素数１の有機ハロゲン化合物、すなわちCF_4　，Cl_2F_2等が分解できるとしているが、フッ素化合物に関する分解結果の実施例はない。また、炭素数１の有機ハロゲン化合物の分解に比べ、一般に炭素数２の有機ハロゲン化合物は分解しにくい。別の例としては、$Al_2O_3-ZrO_2-WO_3$触媒がフッ素化合物ガスの分解触媒として、特開平7－80303号公報に報告されている。この触媒は、フロン類を燃焼分解する触媒であり、フロン－１１５（C_2ClF_5）を処理するのに６００℃で燃焼分解反応を行い、分解率９８％を１０時間保持していた。この方法は燃焼助剤として、ｎ－ブタン等の炭化水素を添加するため、処理コストが大きくなる。また、C_2F_6等の炭素とフッ素のみの化合物の分解は、フロン－１１５に比べ、さらに難しいが、これらの物質に関する分解結果の実施例はない。

【０００６】

【発明が解決しようとする課題】本発明の目的は、炭素を２つ以上含み、フッ素原子を含む化合物、もしくは窒素原子とフッ素原子を含む化合物の少なくとも一方を含むガスを低温で効率よく分解処理する方法及び触媒を提供するものである。

【０００７】

【課題を解決するための手段】本発明者らは、フッ素化合物含有ガスを低温でかつ高効率で分解が可能で、しかも分解生成物として遊離されるフッ化水素による装置の腐食が生じにくい分解処理方法の検討を詳細に進めた結果、本発明に至った。

【０００８】即ち、炭素を２つ以上含み、かつフッ素原子を含む化合物、もしくは窒素原子とフッ素原子を含む化合物の少なくとも一方を含むガス流を、特定のフッ素化合物分解触媒と、約４００～約８００℃の温度で、有効量の水蒸気の存在下で接触させることにより、ガス流

中のフッ素をＨＦに転化できることを見い出した。分解触媒としては、アルミナ，チタニア，シリカ，ジルコニアの少なくとも一種を含む触媒を用いることができる。

【０００９】フッ素化合物としては、C_2F_6などのように炭素数が２以上のＣとＦとの化合物、NF_3 などのＮとＦとの化合物などがある。

【００１０】さらに、触媒にＳｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉのうちの少なくとも一成分を添加すると、フッ素化合物含有ガスをより高い活性で分解できることを見い出した。これらの触媒はアルミナ，チタニア，シリカ，ジルコニア、そしてＳｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉ，Ｐ，Ｂのうちの少なくとも一成分の酸化物を混合物、あるいは複合酸化物の形態で含有している。特にアルミナとチタニアを含む触媒では、アルミナが７５ｗｔ％以上９８ｗｔ％以下、チタニアが２５％以下２ｗｔ％以上である場合に効果が大きい。また、Ｓｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉ，Ｐ，Ｂの酸化物を触媒主量に対して０．１〜１０ｗｔ％ で含む場合に効果が大きい。

【００１１】フッ素化合物含有ガスの分解触媒の開発のため種々検討した結果、触媒の性質として、フッ素と適度な強さの結合を形成する金属成分を含有する必要があることを見い出した。特に、炭素とフッ素とからなる化合物の場合、分子自体が安定であるため、フッ化物生成エンタルピーが大きい金属成分を含有する触媒が高分解活性を示すことを見い出した。あまり安定な結合を形成してしまうと触媒上からフッ素化合物が離れないため、活性が徐々に低下する。一方で結合力が弱すぎると十分な分解率が得られない。本発明の対象ガスであるC_2F_6などは、分子内力が強く、反応性の乏しい物質である。これらのガスを燃焼させる場合、1500〜２０００℃の温度が必要と言われている。我枚は、本対象ガスは、アルミナ，チタニア，シリカ，ジルコニアを単独で触媒として用いても分解できることを見い出したが、より高い分解率を得る触媒としては、アルミナとチタニアを含んでなる触媒が好ましいことを見い出した。アルミナはフッ素化合物を触媒上に引き付ける働きをし、チタニアは触媒上のフッ素化合物を引き離す働きをすると思われる。

【００１２】Ｓｉ，Ｍｇ，Ｚｒ，Ｗ，Ｓｎ，Ｃｅ，Ｍｎ，Ｂｉ，Ｎｉの酸化物は、アルミナ，チタニア，シリカ，ジルコニアとの協奏効果を発現させると思われる。また、触媒中のチタニアの安定化に寄与していると考えられる。

【００１３】本発明のフッ素化合物含有ガスの分解処理方法では、C_2F_6などのフッ素化合物を、不活性ガスで希釈してもよいことを見い出した。フッ素化合物の濃度を希釈することで、触媒に対する負荷が小さくなり、分解活性を長時間維持することができる。希釈ガスとしては、Ａｒ，N_2 ，Ｈｅなどの不活性ガスを用いることができる。

【００１４】本発明の対象とするフッ素含有化合物はC_2F_6，NF_3などのＰＦＣ(perfluorocompound）あるいはＦＦＣ（fully fluorocompound）と呼ばれるもので、代表的な反応としては次のようなものがある。

【００１５】$C_2F_6+3H_2O \rightarrow CO+CO_2+6HF$

$C_2F_6+2H_2O+1/2O_2 \rightarrow 2CO_2+6HF$

$NF_3+3H_2O \rightarrow NO_2+1/2O_2+6HF$

これらのフッ素化合物は、処理するガス中に水素原子をフッ素化合物中のＦ数と少なくとも同等になるよう添加することが望ましい。このことにより、化合物中のＦはＨＦになり、分解生成物中のＦは後処理しやすいハロゲン化水素の形態となる。このときの水素源としては、水蒸気のほかに、水素，炭化水素などを用いることができるが、炭化水素を用いた場合、炭化水素が触媒上で燃焼し、供給する熱エネルギを小さくすることができる。

【００１６】また、反応ガス中に酸素などの酸化ガスを含有させることで、ＣＯの酸化反応も同時に起こらせることができる。ＣＯの酸化反応が不完全な場合は、分解生成ガス中のＨＦを除去した後、ＣＯ酸化触媒に接触させてＣＯをCO_2 に転換させることもできる。

【００１７】本発明の触媒を用いれば、$C_2Cl_3F_3$，$C_2Cl_2F_4$，C_2ClF_5などのフロン類，ＨＦＣ１３４ａなどの代替フロン類、また、SF_6 等の化合物も分解できる。また、CCl_3F ，CCl_2F_2などの物質も十分分解できる。なお、塩素化合物を処理した場合の化合物中のＣｌは、ＨＣｌに転化される。

【００１８】本発明で用いられる反応温度は、約４００〜約８００℃が好ましい。これ以上の高温で使用すると、高分解率は得られるが、触媒の劣化が速い。また、装置材料の腐食速度が急激に大きくなる。逆に、これ以下の温度では、分解率が低い。また、生成したＨＦを中和除去する工程としては、アルカリ溶液をスプレーして洗浄するものが効率が高く、結晶析出などによる配管の閉塞が起こりにくいので好ましい。アルカリ溶液中に分解生成ガスをバブリングする方法あるいは充填塔を用いて洗浄する方法でもよい。

【００１９】本発明の触媒を調製するためのＡｌ原料としては、γ−アルミナ，γ−アルミナとδ−アルミナの混合物などを使用することができる。特にベーマイトなどをＡｌ原料として用い、最終的な焼成により酸化物を形成するのも好ましい方法である。

【００２０】本発明の触媒を調製するためのＴｉ原料としては、硫酸チタン，チタニアゾル，チタンスラリ、などを使用することができる。

【００２１】さらに、Ｓｉ，Ｍｇ，Ｚｒなどの第三金属成分の原料としては、各種、硝酸塩，アンモニウム塩，塩化物などを用いることができる。

【００２２】本発明の触媒の製造法は通常触媒の製造に用いられる沈殿法，含浸法，混練法などいずれも使用で

きる。

【００２３】また、本発明における触媒は、そのまま粒状，ハニカム状などに成形して使用することができる。成形法としては、押し出し成形法，打錠成形法，転動造粒法などを目的に応じ任意の方法を採用できる。また、セラミックスや金属製のハニカムや板にコーティングして使用することもできる。

【００２４】本発明のフッ素化合物含有ガス処理方法は、他の処理方法に比べて低温でフッ素化合物を分解することができる。

【００２５】フッ素化合物含有ガスを処理する場合、分解して生成するＨＦなどの酸成分による装置材料の腐食が問題となるが、本発明によれば、使用する温度が比較的低温であるため、腐食速度が遅く、装置のメンテナンスなどが不要となる。

【００２６】本発明のフッ素化合物含有ガス処理方法を実施する装置は、フッ素化合物を分解する触媒反応槽と分解生成ガス中の酸成分を中和除去する設備を備えるだけでよく、装置を小型化できる。

【００２７】

【発明の実施の形態】以下、実施例にて本発明をさらに詳細に説明する。本発明は、これら実施例にのみ限定されるものではない。

【００２８】図１は、本発明の分解処理方法を半導体生産プロセスのプラズマＣＶＤ装置のクリーニング工程で用いる場合の実施例を示す。

【００２９】プラズマＣＶＤ装置は、半導体ウェハー表面にSiO_2 膜を蒸着法で形成させる装置である。しかし、SiO_2 膜は装置内全体に付着してしまうので、不必要な箇所に付いたSiO_2 を除去する必要がある。このSiO_2 をクリーニングするためにC_2F_6が用いられる。C_2F_6を含むクリーニングガスは、ＣＶＤチャンバへ送られ、プラズマで励起してSiO_2を除去する。その後、チャンバ内をN_2で置換し、C_2F_6濃度を約３～５％に希釈して約１５ｌ／min でチャンバから排出している。

【００３０】この排出ガスに空気３を添加しC_2F_6を希釈した。この希釈ガスに、さらに水蒸気４を添加した反応ガス５を分解工程に送る。反応ガス中のC_2F_6濃度は約０.５％ である。分解工程では、反応ガス５を、空間速度３０００毎時（空間速度（h^1）＝反応ガス流量（ｍｌ／ｈ）／触媒量（ｍｌ））の条件でAl_2O_3系触媒と７００℃で接触させる。この場合、反応ガスを加熱してもよく、電気炉などにより触媒を加熱してもよい。分解ガス６は、排ガス洗浄工程に送られる。排ガス洗浄工程では、分解ガス６にアルカリ水溶液がスプレーされ、分解ガス中の酸成分が除去された排ガス７が系外に放出される。C_2F_6の分解率は、反応ガス５と排ガス７をＦＩＤ（Flame Ionization Detector の略称）ガスクロマトグラフ，ＴＣＤ（Thermal Conductivity Detector の略称）ガスクロマトグラフを用いて分析し、入り口及び出口の物質収支により求める。

【００３１】以下、各種フッ素化合物分解触媒の活性を調べた結果について説明する。

【００３２】［実施例１］純度９９％以上のC_2F_6ガスに空気を添加して希釈した。この希釈ガスに、さらに水蒸気を添加した。水蒸気は純水を０.１１ｍｌ／minで反応管上部へマイクロチューブポンプを用いて供給しガス化させた。反応ガス中のC_2F_6濃度は約０.５％ であった。この反応ガスを、電気炉により反応管外部から７００℃に加温した触媒と空間速度３０００毎時で接触させた。

【００３３】反応管は内径１９㎜のインコネル製の反応管で、触媒層を反応管中央に有しており、内部に外径３㎜のインコネル製の熱電対保護管を有している。触媒層を通過した分解生成ガスは水酸化ナトリウム溶液中にバブリングさせ、系外に放出した。C_2F_6の分解率は、ＦＩＤガスクロマトグラフ，ＴＣＤガスクロマトグラフにより、次式で求めた。

【００３４】

【数１】

$$\text{分解率} = 1 - \frac{\text{出口のフッ素化合物}}{\text{供給したフッ素化合物}} \times 100\ (\%) \qquad \cdots(\text{数}1)$$

【００３５】以下に上記条件における試験に供した各触媒の調製法を示す。

【００３６】触媒１；Al_2O_3

住友化学製粒状アルミナ（ＮＫＨＤ－２４）を粉砕し、０.５－１㎜ 粒径に篩い分けし、１２０℃で２時間乾燥し、７００℃で２時間焼成したものを試験に供した。

【００３７】触媒２；TiO_2

堺化学製粒状チタニア（ＣＳ－２００－２４）を粉砕し、０.５－１㎜ 粒径に篩い分けし、１２０℃で２時間乾燥し、７００℃で２時間焼成したものを試験に供した。

【００３８】触媒３；ZrO_2

硝酸ジルコニル２００ｇを１２０℃で２時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１㎜ 粒径のジルコニアに造粒し、試験に供した。

【００３９】触媒４；SiO_2

Fuji Silysia製粒状シリカ（ＣＡＲＩＡＣＴ－１０）を粉砕し、０.５－１㎜粒径に篩い分けし、１２０℃で２時間乾燥し、７００℃で２時間焼成したものを試験に供した。

【００４０】触媒５；TiO_2-ZrO_2

堺化学製粒状チタニア（ＣＳ－２００－２４）を０.５mm以下に粉砕した。この粉末１００ｇに対し硝酸ジルコニル７８.３ｇを加え、純水を添加しながら混練した。混練後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm粒径に造粒し、試験に供した。

【００４１】触媒６；Al_2O_3-MgO

住友化学製粒状アルミナ（ＮＫＨＤ－２４）を０.５mm以下の粒径に粉砕した。この粉末１００ｇに対し、硝酸マグネシウム５６.４ｇを加え、純水を添加しながら混練した。混練後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm粒径として試験に供した。

【００４２】触媒７；$Al_2O_3-TiO_2$

住友化学製粒状アルミナ（ＮＫＨＤ－２４）を０.５mm以下の粒径に粉砕した。この粉末１００ｇに対し、メタチタン酸スラリの乾燥粉末５６.４ｇを加え、純水を添加しながら混練した。混練後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm粒径として試験に供した。

【００４３】触媒８；$Al_2O_3-SiO_2$

住友化学製粒状アルミナ（ＮＫＨＤ－２４）を０.５mm以下の粒径に粉砕した。この粉末１００ｇに対し、SiO_2ゾルの乾燥粉末１３.２ｇを加え、純水を添加しながら混練した。混練後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm粒径として試験に供した。

【００４４】上記触媒１～８の試験結果を図２に示す。

【００４５】［実施例２］本実施例は、実施例１と同様の条件で、第三成分添加の効果を調べたものである。各触媒は以下のように調製した。

【００４６】触媒９；$Al_2O_3-TiO_2$

住友化学製粒状アルミナ（ＮＫＨＤ－２４）を粉砕し、０.５－１mm粒径に篩い分けし、１２０℃で２時間乾燥した。これに、３０％硫酸チタン溶液１７６ｇを含浸した。含浸後、２５０～３００℃で約５時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００４７】触媒１０；$Al_2O_3-TiO_2-ZrO_2$

住友化学製粒状アルミナ（ＮＫＨＤ－２４）を粉砕し、０.５－１mm粒径に篩い分けし、１２０℃で２時間乾燥した。これに、３０％硫酸チタン溶液１７６ｇを含浸した。含浸後、２５０～３００℃で約５時間乾燥し、７００℃で２時間焼成し、触媒Ａを作製した。続いて、触媒Ａ５０ｇに、硝酸ジルコニル２水和物６.７ｇを９０ｇのH_2Oに溶かした水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００４８】触媒１１；$Al_2O_3-TiO_2-WO_3$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、パラタングステン酸アンモニウム６.５ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００４９】触媒１２；$Al_2O_3-TiO_2-SiO_2$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、２０wt％シリカゾル７.５ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

触媒１３；$Al_2O_3-TiO_2-SnO_2$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、塩化すず２水和物５.６ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、120℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００５０】触媒１４；$Al_2O_3-TiO_2-CeO_2$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、硝酸セリウム６水和物１０.９ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

触媒１５；$Al_2O_3-TiO_2-MnO_2$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、硝酸マンガン６水和物７.２ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００５１】触媒１６；$Al_2O_3-TiO_2-Bi_2O_3$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、硝酸ビスマス６水和物７.４ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００５２】触媒１７；$Al_2O_3-TiO_2-NiO$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、硝酸ニッケル６水和物７.３ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成した。これを試験に供した。

【００５３】触媒１８；$Al_2O_3-TiO_2-BO_4$

触媒１０と同様の方法で触媒Ａを作製した。続いて、触媒Ａ５０ｇに、ほう酸アンモニウム８水和物１２.０ｇをH_2Oに溶かした９０ｇの水溶液を含浸した。含浸後、１２０℃で２時間乾燥し、７００℃で２時間焼成し

た。これを試験に供した。

【００５４】上記触媒９～１８と、実施例１中の触媒１の活性を図３に示す。

【００５５】［実施例３］本実施例は、アルミナ原料及びチタニア原料を変化させて各種触媒を調製し、実施例１と同様の方法で活性を調べた例である。

【００５６】触媒１９；Al_2O_3
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で２時間乾燥した。この乾燥粉末２００ｇを３００℃で０.５時間焼成し、さらに焼成温度を７００℃にあげ２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^{2}の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。

【００５７】触媒２０；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末２００ｇと３０％硫酸チタン溶液２４８.４ｇ を純水約２００ｇを添加しながら混練した。混練後、２５０～３００℃で約５時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。

【００５８】触媒２１；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末２００ｇと、３０％チタニアゾル７８.６ｇ に純水を加えた約１００ｇの水溶液を混練した。混練後、１２０℃で約２時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。上記の触媒１９～２１の活性を実施例１と同様の方法で調べた結果を図４に示す。

【００５９】［実施例４］本実施例は、実施例３の触媒２０中のＡｌとＴｉの組成を変化させた触媒を調製し、活性を調べた結果である。

【００６０】触媒２２；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末１００ｇと３０％硫酸チタン溶液４８.８ｇ を純水約１５０ｇを添加しながら混練した。混練後、２５０～３００℃で約５時間乾燥し、700℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。

【００６１】触媒２３；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末１００ｇと３０％硫酸チタン溶液８２.４ｇ を純水約１２０ｇを添加しながら混練した。混練後、２５０～３００℃で約５時間乾燥し、700℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。

【００６２】触媒２４；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末１００ｇと３０％硫酸チタン溶液１７４.４ｇ を純水約７０ｇを添加しながら混練した。混練後、２５０～３００℃で約５時間乾燥し、700℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。

【００６３】触媒２５；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末１００ｇと３０％硫酸チタン溶液３９２ｇを添加しながら混練した。混練後、２５０～３００℃で約５時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。

【００６４】上記の触媒２２～２５の活性を実施例１と同様の方法で調べた結果を図５に示す。

【００６５】［実施例５］本実施例は、触媒調製時に硫酸を添加した場合の例である。

【００６６】触媒２６；$Al_2O_3-TiO_2$
ＣＯＮＤＥＡ製ベーマイト粉末（ＰＵＲＡＬ　ＳＢ）を１２０℃で１時間乾燥した。この乾燥粉末１５０ｇに、石原産業製ＣＳ－Ｎ３０％チタニアゾル溶液５８.８ｇと、９７％硫酸溶液４４.８ｇ を純水２５０ｍｌで希釈した水溶液を添加し混練した。混練後、２５０～３００℃で約５時間乾燥し、７００℃で２時間焼成した。得られた粉末を金型に入れ、５００kgf／cm^2 の圧力で圧縮成型した。成型品を粉砕，篩い分けして０.５－１mm 粒径として試験に供した。試験条件は、空間速度を１０００毎時とした以外は実施例１と同様である。試験の結果、反応温度６５０℃でC_2F_6の分解率８０％が得られた。

【００６７】

【発明の効果】本発明によれば、C_2F_6，NF_3 などのフッ素含有ガスを効率良く分解処理することができる。

【図面の簡単な説明】

【図１】本発明の一実施例による処理プロセスを示す工程図である。

【図２】各種フッ素化合物分解触媒の性能を示すグラフである。

【図３】各種フッ素化合物分解触媒の性能を示すグラフである。

【図４】各種フッ素化合物分解触媒の性能を示すグラフである。

【図５】各種フッ素化合物分解触媒の性能を示すグラフ

である。

【符号の説明】

１…C_2F_6、２…N_2、３…空気、４…水蒸気、５…反応ガス、６…分解ガス、７…排ガス。

【図１】

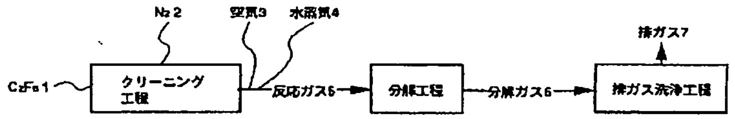
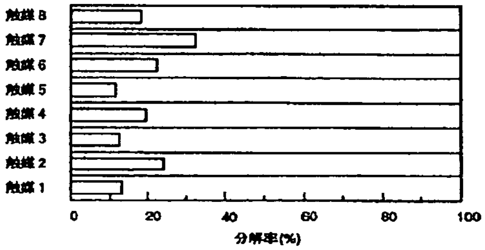


図 1

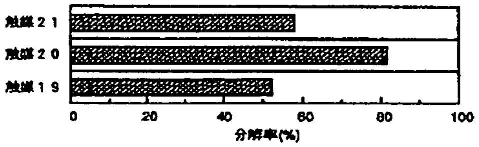
【図２】

図 2



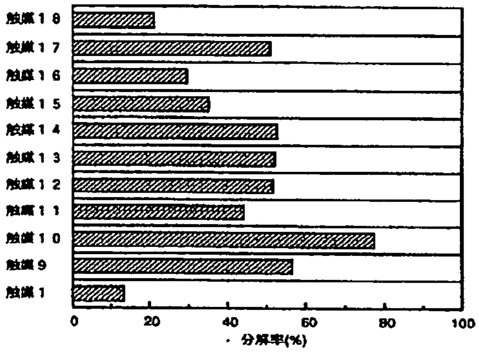
【図４】

図 4



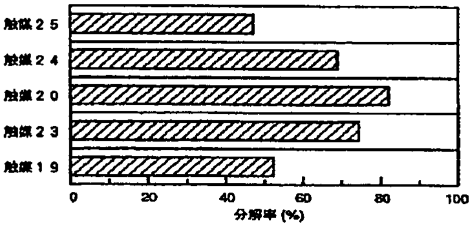
【図３】

図 3



【図５】

図 5



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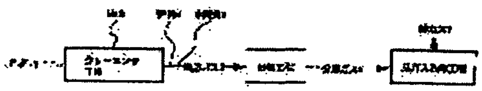
(54) TREATMENT OF GAS CONTAINING FLUORINE COMPOUND

(57)Abstract:

PROBLEM TO BE SOLVED: To decompose gas containing fluorine compounds efficiently at low temperatures by contacting a gas flow containing at least one of a compound consisting of two or more carbon atoms and fluorine atoms and a compound consisting of nitrogen atoms and fluorine atoms with a specified fluorine compound decomposition catalyst in the presence of water vapor.

SOLUTION: When implemented in the plasma CVD apparatus-cleaning process of a semiconductor production process, cleaning gas containing C2F6 1 which was used for removing Si02 is sent into a CVD chamber and exited by plasma to remove Si02. After that, the chamber is replaced with N2 2, C2F6 concentration is reduced to about 3-5%, and gas is discharged. Reaction gas 5 in which the exhaust gas is added with air 3 and water vapor 4 is sent to a



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decomposition process, in which the gas 5 is contacted with an A1203 catalyst at 400-800° C. Next, decomposition gas 6 is sent to an exhaust gas washing process, in which an alkali aqueous solution is sprayed, and exhaust gas 7 in which acid component in the decomposition gas 6 is eliminated is released outside the system.

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DECLARATION

I, Kazuhiro ISHII , a national of Japan, c/o Asamura Patent Office of 331-340, New Ohtemachi Building, 2-1, Ohtemachi-2-chome, Chiyoda-ku, Tokyo, Japan do hereby solemnly and sincerely declare:

1) THAT I am well acquainted with the Japanese language and English language, and
2) THAT the attached is a full, true, accurate and faithful translation into the English language made by me of JP-A-10-192653.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 24th day of February , 2006 .

Kazuhiro ISHII

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Continued to the last page

(54) [Title of the Invention]

PROCESS FOR TREATING FLUORINE COMPOUND-CONTAINING GAS

(57) [Abstract]

[Problem]

To provide a decomposition treatment process for decomposing fluorine compound-containing gas such as C_2F_6 and the like efficiently and catalyst therefore.

[Solution]

A gas stream containing at least one of compounds having two or more carbon atoms and fluorine atom(s) such as C_2F_6 and the like, or compounds of nitrogen atom(s) and fluorine atom(s) is contacted with a catalyst comprising at least one of alumina, titania, silica and zirconia at a temperature of about 400° to about 800°C in the presence of an effective amount of water vapor to convert F in the gas stream to HF.

[Advantages]

Fluorine compound-containing gas can be subjected to decomposition treatment with good efficiency.

Fig. 2

[Claims]

[Claim 1]

A process for treating a fluorine compound-containing gas, characterized by containing a step of contacting a gas stream containing at least one of a compound including two or more carbon atoms and fluorine atom(s), or a compound containing nitrogen atom(s) and fluorine atom(s) with a catalyst containing at least one of alumina, titania, silica and zirconia at a temperature of about 400 to 800°C in the presence of an effective amount of water vapor to convert the F in the gas stream to HF.

[Claim 2]

The process according to Claim 1, wherein the fluorine compound-containing gas includes a compound of C and F having two or more carbon atoms, or a compound of N and F.

[Claim 3]

The process according to Claim 1, wherein the catalyst further contains at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni.

[Claim 4]

A catalyst for decomposing fluorine compounds by treating a gas stream containing at least one of a compound of C and F having two or more carbon atoms, or a compound of N and F, said catalyst comprising alumina and titania, wherein the alumina is contained 75% by weight or more and 98% by weight or less, and the titania is contained 25% by weight or less and 2% by weight or more.

[Claim 5]

The catalyst according to Claim 4, wherein the catalyst further contains at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B.

[Claim 6]

The catalyst according to Claim 5, wherein the catalyst contains one or more oxides of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B in an amount of 0.1% by weight to 10% by weight based on the main weight of the aluminatitania catalyst.

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a process for efficient decomposition treatment of a gas containing fluorine compounds such as C_2F_6, etc. at a low temperature and a catalyst material.

[0002]

[Prior Art]

Fluorine compound gases such as C_2F_6, etc. are used in a large amount as a semiconductor etchant, a semiconductor cleaner, etc. However, it was found that these compounds, once discharged into the atmosphere, turn into warming substances causing global warming. Post-treatment of these compounds after their use wouldbe subject to a strict control in the future.

[0003]

By the way, gases such as C_2F_6, etc. have fluorine (F) in a large amount as a molecular constituting element. The fluorine is the highest in electronegativity among all the elements and forms chemically very stable substances. Particularly, C_2F_6 and the like are strong in intramolecular force and substances poor in reactivity. From these properties, a high temperature is necessary for decomposition and a large amount of energy is consumed therefor. Further, the decomposition reaction at the high temperature produces gases such as hydrogen fluoride, etc. which are large in corrosion rate of apparatus materials. It is thus in the current situations that no appropriate processes for such decomposition treatment are not available yet.

[0004]

As the decomposition treatment processes, there is proposing a combustion technology at a high temperature. But, according to this process, since a large amount of fuel is used, the energy efficiency is low. In addition, there is a problem of damage of furnace wall caused by halogen compounds produced by combustion at 1000°C or higher. Therefore, it is necessary a technology which can decompose at lower temperatures.

[0005]

As to the catalyst, JP-B-6-59388 discloses a TiO_2-WO_3 catalyst for decomposition of organic halogen compounds. The catalyst contains 0.1 to 20% by weight of W on the basis of TiO_2 (i.e. 92% to 99.96% of Ti by atom and 8 to 0.04% by atom of W) and had a decomposition rate of 99% at 375°C for a duration of 1,500 hours in treatment of CCl_4 in ppm order. Among organic halogen compounds, influences as catalyst poison are found not only in Cl but also in F, the latter is greater than the former. JP-B-6-59388 suggests that organic halogen compounds having a single carbon atom, such as CF_4, CCl_2F_2, etc. can be decomposed, but shows no examples of decomposition results of fluorine compounds. Further, generally speaking, organic halogen compounds having 2 carbon atoms are less decomposable than those having a
single carbon atom.

JP-A-7-80303 discloses another Al_2O_3-ZrO_2-WO_3 catalyst for decomposition of fluorine compound gases. The catalyst is directed to combustion-decomposition of CFCs (chlorofluorocarbons) and has a decomposition rate of 98% for a duration of 10 hours in treatment of CFC-115 (C_2ClF_5) by combustion-decomposition reaction at 600°C. The disclosed process needs addition of hydrocarbons such as n-butane, etc. as a combustion aid, resulting in a higher treatment cost. Decomposition of compounds consisting only of carbon and fluorine such as C_2F_6, etc. are much less decomposable than CFC-115, but no examples of decomposition results of such compounds are shown therein.

[0006]

[Problem to be Solved by the Invention]

An object of the present invention is to provide a process for efficient decomposition treatment of a gas containing at least one of a compound having two or more carbon atoms and fluorine atom(s), or a compound having nitrogen atom(s) and fluorine atom(s) at a low temperature, and a catalyst therefore.

[0007]

[Means for Solving Problem]

The present inventors have studied decomposition treatment processes which are possible to decompose fluorine compound-containing gas at low temperatures with high efficiency and hardly provide corrosion of the apparatus by hydrogen fluoride freed as a decomposition product, and as a result, the present invention is attained.

[0008]

That is, it was found that by contacting a gas stream containing at least one of a compound having two or more carbon atoms and fluorine atom(s), or a compound having nitrogen atom(s) and fluorine atom(s) with a catalyst for decomposing specific fluorine compounds at about 400 to about 800°C in the presence of an efficient amount of water vapor, the fluorine in the gas stream can be converted to HF. As the decomposing catalyst, it is possible to use a catalyst which contains at least one kind selected from alumina, titania, silica and zirconia.

[0009]

As the fluorine compounds, there can be used those having C and F with two or more carbon atoms such as C_2F_6, etc., those having N and F such as NF_3, etc.

[0010]

Further, it was found that when at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni is added to the catalyst, it was possible to decompose the fluorine compound-containing gas with higher activity. These catalysts contains alumina, titania, silica, zirconia and oxide or oxides of at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B in the form of a mixture or composite oxide. In the case of the catalyst containing alumina and titania, when alumina is 75% by weight or more and 98% by weight or less and titania is 25% by weight or less and 2% by weight or more, the effects are very great. Further, when the oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P, and B is contained 0.1 to 10% by weight based on the main weight of the catalyst, the effects are great.

[0011]

As a result of various studies for developing decomposition catalysts for fluorine compound-containing gas, it was found that it is necessary to contain a metallic component for forming a bond to fluorine with a suitable strength. Particularly, in the case of a compound containing carbon and fluorine, since the molecule per se is stable, it was found that a catalyst containing a metallic component having a large fluoride forming enthalpy shows a high decomposition activity. When a too stable bond is formed, the activity lowers gradually because of non-release of the fluoride from the catalyst surface. On the other hand, when the bonding strength is too weak, a sufficient decomposition rate cannot be obtained. The gases used in the present invention such as C_2F_6 or the like are substances which have a strong intramolecular force and poor reactivity. In order to combust these gases, the temperature of 1500 to 2000°C is said to be necessary. We have found that the gases used in the present invention can be decomposed by even using alumina, titania, silica and zirconia singly as a catalyst, and in order to obtain higher decomposition rate, it is preferable to use a catalyst containing alumina and titania. The alumina seems to function for drawing the fluorine compound to the catalyst and the titania seems to function for separating the fluorine compound from the catalyst surface.

[0012]

The oxides of Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni seem to exhibit synergistic effects with alumina, titania, silica and zirconia. Further, the titania in the catalyst seems to contribute to the stabilitation.

[0013]

In the decomposition treatment process of the fluorine compound-containing gas of the present invention, it was found that the fluorine compound such as C_2F_6 or the like can be diluted with an inert gas. By diluting the concentration of the fluorine compound, the load for the catalyst is reduced, resulting in maintaining the decomposition activity for a long period of time. As the diluting gas, it is possible to use an inert gas such as Ar, N_2, He or the like.

[0014]

The fluorine-containing compounds used in the present invention are PFC (perfluorocompounds) such as C_2F_6, NF_3, etc. or FFC (fully fluorocompounds). Typical reactions can be shown below.

[0015]

$$C_2F_6 + 3H_2O \rightarrow CO + CO_2 + 6HF$$

$C_2F_6 + 2H_2O + 1/2O_2 \rightarrow 2CO_2 + 6HF$

$NF_3 + 3H_2O \rightarrow NO_2 + 1/2\ O_2 + 6HF$

It is desirable to add these fluorine compounds so as to make the amount of hydrogen atoms in the gas to be treated at least equal to the amount of fluorine atoms contained in the fluorine compound. By this, F in the compound becomes HF, and F in the decomposition products changes into hydrogen halide which is easy for after-treatment. As a hydrogen source, there can be used steam, hydrogen, a hydrocarbon, etc. In the case of using a hydrocarbon, the hydrocarbon can be combusted on the catalyst, thereby effectively reducing the heat energy to be supplied.

[0016]

By adding an oxidizing gas such as oxygen, etc. to the reaction gas, oxidation reaction of CO can be carried out at the same time. When the oxidation reaction of CO is incomplete, the decomposition product gas is brought into contact with the CO oxidizing catalyst, after removal of HF from the decomposition product gas, to convert CO to CO_2.

[0017]

By using the catalyst of the present invention, flons such as $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5, etc., substitute flons such as HFC 134a, etc. and compounds such as SF_6, etc. can be decomposed. Further, Cl in the compounds in the case of treating chlorine compounds is converted to HCl.

[0018]

The reaction temperature used in the present invention is preferably about 400° to about 800°C. Above the higher temperatures, a higher decomposition rate can be obtained, but the catalyst will be rapidly deteriorated, and also the corrosion rate of apparatus structural materials will be abruptly increased, whereas below the lower temperature, the decomposition rate will be lowered.

As the step of neutralizing and removing the formed HF, washing by spraying an alkaline solution is efficient and preferable because of less occurrence of clogging in pipes due to crystal deposition, etc. Bubbling of the decomposition product gas through the alkaline solution or washing with the alkaline solution through a packed column may be used.

[0019]

As the raw material for aluminum (Al) for preparing the catalyst of the present invention, γ-alumina and a mixture of γ-alumina and δ-alumina can be used. Particularly preferable method is to use boehmite, etc. as a raw material for Al to form an oxide through final firing.

[0020]

As the raw material for titanium (Ti) for preparing the catalyst of the present invention, there can be used titanium sulfate, titania sol, titanium slurry, etc.

[0021]

Further, as raw materials for the third metallic components such as silica (Si), magnesium (Mg), zirconium (Zr), etc., their various nitrates, ammonium salts, chlorides, etc. can be used.

[0022]

The catalyst of the present invention can be prepared by any of ordinary procedures for preparing catalysts, such as a precipitation method, an impregnation method, a kneading method, etc.

[0023]

The catalyst of the present invention can be used as such or upon molding into a granular form, a honeycomb form, etc. by a desired molding procedure such as extrusion molding, tabletting, tumbling granulation, etc., or as a coating on ceramic or metallic honeycombs or plates.

[0024]

The fluorine compound-containing gas treating process of the present invention can decompose the fluorine compounds in a lower temperature than other treating processes.

[0025]

In the case of treating fluorine compound-containing gas, there arises a problem of corrosion of apparatus materials caused by the acid component such as HF, etc. produced by decomposition. According to the present invention, since the temperature used is relatively low, the corrosion rate is slow, resulting in unnecessary for maintenance of the apparatus.

[0026]

The apparatus for practicing the fluorine compound-containing gas treating process of the present invention requires only a catalytic reactor for decomposing the fluorine compounds and an apparatus for neutralizing and removing acid components in the decomposition product gas, so that the apparatus can be minimized.

[0027]

[Mode for Carrying Out the Invention]

The present invention will be described in detail below, referring to Examples which are not limitative of the present invention.

[0028]

Fig. 1 shows an example of using the decomposition treatment process of the present invention fir a cleaning step in a plasma CVD apparatus in the semiconductor production process.

[0029]

The plasma CVD apparatus is an apparatus for vapor depositing a SiO_2 film on a semiconductor wafer surface. Since the SiO_2 film tends to deposit on the entire interior surfaces of the apparatus, and thus it is necessary to remove SiO_2 depositions from unwanted surfaces. To clean the SiO_2, C_2F_6 is used. Cleaning gas containing C_2F_6 is led to a CVD chamber to remove SiO_2 under plasma excitation. Then, the chamber is flushed with a N_2 gas, thereby diluting the concentration of C_2F_6 to about 3 to 5%, followed by discharge from the chamber at about 15 l./min.

[0030]

The discharged gas is admixed with air 3 to dilute C_2F_6. The diluted gas is further admixed with steam 4 to give a reaction gas 5, which is led to a decomposition step. The C2F6 concentration in the reaction gas is about 0.5%. In the decomposition step, the reaction gas 5 is contacted with a Al_2O_3 series catalyst at 700°C under the conditions of space velocity of 3000 per hour [space velocity (h^{-1}) = reaction gas flow rate (ml/h)/catalyst volume (ml)]. In that case, the reaction gas may be heated or the catalyst may be heated by an electric oven, etc. The resulting decomposition gas 6 is led to an exhaust gas washing step, where the decomposition gas 6 is sprayed with an aqueous alkaline solution to remove acid components from the decomposition gas 6 and the resulting exhaust gas 7 freed from the acid components is discharged to the system outside. The decomposition rate of C_2F_6 is obtained from the analysis data of the reaction gas 5 and the exhaust gas 7 using FID (flame ionization detector) gas chromatograph and TCD (thermal conductivity detector) gas chromatograph, and material balance at the inlet and the outlet.

[0031]

Hereinafter, the results obtained by examining activities of various fluorine compound decomposing catalysts are explained.

[0032]

[Example 1]

A C_2F_6 gas having a purity of 99% or more was diluted with air, and further admixed with steam to prepare a reaction gas. Steam for the admixture was prepared by feeding pure water into a reactor tube from the top at a flow rate of 0.11 ml/min. by a microtube pump and gasified. The reaction gas had a C_2F_6 concentration of about 0.5%. Then, the reaction gas was brought into contact with various catalysts heated to 700°C in the reactor tube at a space velocity of 3,000 h^{-1}.

[0033]

The reactor tube is a reactor tube manufactured by Inconel and having an inner diameter of 19 mm, where a catalyst bed is fixed at the center of the reactor tube and had an Inconel-made thermowell for a thermo couple, 3 mm in outer diameter, inside the catalyst bed. Decomposition product gas discharged from the catalyst bed was bubbled through an aqueous sodium chloride solution an then discharged as an exhaust gas. C_2F_6 decomposition rate was calculated by the following equation using FID gas chromatograph and TCD gas chromatograph:

[0034]

[Expression 1]

$$\text{Decomposition rate} = 1 - \frac{\text{Concentration of discharged fluorine compound}}{\text{Concentration of fed fluorine compound}} \times 100\ (\%)$$

[0035]

Hereinafter, preparation methods of various catalysts used for the tests under the above-mentioned conditions are shown.

[0036]

Catalyst 1 : Al_2O_3

Granular alumina (NKHD-24, trademark of a product commercially available from Sumitomo Chemical Co., Ltd., Japan) was pulverized, sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing (or calcining) at 700°C for 2 hours, and subjected to the tests.

[0037]

Catalyst 2 : TiO_2

Granular titania (CS-200-24, trademark of a product commercially available from Sakai Chemical Industry Co., Ltd., Japan) was pulverized, sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing at 700°C for 2 hours, and subjected to the tests.

[0038]

Catalyst 3 : ZrO_2

200 g of zirconyl nitrate was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain zirconia grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0039]

Catalyst 4 : SiO_2

Granular silica (CARIACT-10, trademark of a product commercially available from Fuji Silysia Co., Ltd., Japan) was pulverized and sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing at 700°C for 2 hours, and subjected to the tests.

[0040]

Catalyst 5 : TiO_2-ZrO_2

Granular titania (CS-200-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders was admixed with 78.3 g of zirconyl nitrate and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0041]

Catalyst 6 : Al_2O_3-MgO

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 56.4 g of magnesium nitrate and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0042]

Catalyst 7 : Al_2O_3-TiO_2

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 17.4 g of dried powders of a metatitanic acid slurry and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0043]

Catalyst 8 : Al_2O_3-SiO_2

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 13.2 g of dried powders of SiO_2 sol and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 mgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0044]

Test results of the above-mentioned catalysts 1 to 8 are shown in Fig. 2.

[0045]

[Example 2]

In this Example, effects of addition of the third elements were examined under the same conditions as in Example 1. Individual catalysts were prepared as follows.

[0046]

Catalyst 9 : Al_2O_3-TiO_2

Granular alumina (NKHD-24) was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, followed by drying at 120°C for 2 hours. Then, the dried grains were impregnated with 176 g of an aqueous 30% titanium sulfate solution. After the impregnation, the grains were dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0047]

Catalyst 10 : Al_2O_3-TiO_2-ZrO_2

Granular alumina (NKHD-24) was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, followed by drying at 120°C for 2 hours. Then, the dried grains were impregnated with 176 g of an aqueous 30% titanium sulfate solution. After the impregnation, the grains were dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours, to give Catalyst A. Then, 50 g of Catalyst A grains were impregnated with an aqueous solution of 6.7 g of zirconyl nitrate dihydrate in 90 g of H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0048]

Catalyst 11 : Al_2O_3-TiO_2-WO_3

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 6.5 g of ammonium paratungstate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0049]

Catalyst 12 : Al_2O_3-TiO_2-SiO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.5 g of 20 wt.% silica sol in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

Catalyst 13 : Al_2O_2-TiO_2-SnO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 5.6 g of tin chloride dihydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0050]

Catalyst 14 : Al_2O_3-TiO_2-CeO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 10.9 g of cerium nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

Catalyst 15 : Al_2O_3-TiO_2-MnO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.2 g of manganese nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0051]

Catalyst 16 : Al_2O_3-TiO_2-Bi_2O_3

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.4 g of bithmus nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0052]

Catalyst 17 : Al_2O_3-TiO_2-NiO

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.3 g of nickel nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0053]

Catalyst 18 : Al_2O_3-TiO_2-BO_4

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 12.0 g of ammonium borate octahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0054]

Activities of the above-mentioned Catalysts 9-18 as well as that of Catalyst 1 in Example 1 are shown in Fig. 3.

[0055]

[Example 3]

In this Example, various catalysts are prepared by changing the alumina raw material and the titania raw material, and activities are examined in the same manner as in Example 1.

[0056]

Catalyst 19 : Al_2O_3

Boehmite powders (PURAL SB, trademark of a product commercially available from Condea Co., Ltd.) were dried at 120°C for 2 hours. 200 g of the resulting dried powders were fired at 300°C for 0.5 hour and further fired at an elevated temperature of 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and tested.

[0057]

Catalyst 20 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 200 g of the resulting dried powders were kneaded with 248.4 g of an aqueous 30% titanium sulfate solution, while adding about 200 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0058]

Catalyst 21 : AlO_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 200 g of the resulting dried powders were kneaded with about 100 g of an aqueous solution containing 78.6 g of 30% titania sol in pure water. After the kneading, the kneaded mixture was dried at 120°C for about 2 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0059]

[Example 4]

In this Example, catalysts are prepared by changing the composition of Al and Ti in Catalyst 20 in Example 3 and their activities are examined.

[0060]

Catalyst 22 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 48.8 g of an aqueous 30% titanium sulfate solution while adding about 150 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0061]

Catalyst 23 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 82.4 g of an aqueous 30% titanium sulfate solution while adding about 120 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0062]

Catalyst 24 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 174.4 g of an aqueous 30% titanium sulfate solution while adding about 70 g of pure water. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0063]

Catalyst 25 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) was dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 392g of 30% titania sol. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0064]

Activities of the above-mentioned Catalysts 22-25 are examined in the same manner as in Example 1 and the results are shown in Fig. 5.

[0065]

[Example 5]

In this Example, sulfuric acid is added at the time of preparing a catalyst.

[0066]

Catalyst 26: Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 150 g of the resulting dried powders, 58.8 g of 30% titania sol solution (CS-N, manufactured by Ishihara Sangyo Kaisha, Ltd.) and an aqueous solution of 44.8 g of 97% sulfuric acid solution diluted with 250 ml of pure water were added and kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The test conditions are the same as those of Example 1, except for changing the space velocity 1000 per hour. The test results were that the decomposition rate of C_2F_6 at the reaction temperature of 650°C was 80%.

[0067]

[Effects of the Invention]

Continued from the front page

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